

Miscibility of Mixed Stereoregular PMMA/PVAc Monolayers at the Air/water Interface

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ABSTRACT

The mixed monolayer behavior of stereoregular poly(methyl methacrylate) (PMMA) and poly(vinyl acetate) (PVAc) was investigated from the measurements of surface pressure-area per molecule (π -A) isotherms at three different temperatures. Miscibility deduced from the π -A isotherms of mixed stereoregular PMMA/PVAc monolayer correlates approximately with that for the corresponding polymer blends in the bulk state. The miscibility and nonideality of the mixed monolayers were examined by calculating the excess area as a function of composition. Positive and negative deviations from ideality were observed. Negative deviations observed at high PVAc compositions might suggest that the existence of favorable interactions between PMMA and PVAc. Conversely, positive deviations indicated that the existence of unfavorable interactions. Interestingly, the A_{ex}/A_{id} values were found to be often negative at a high PVAc mole fraction. The miscibility between PVAc and PMMA is therefore proven possible at this composition in the two-dimensional state.

1. INTRODUCTION

Polymer blends in the thin film states are of special interest for both

fundamental studies and practical applications. There are lots of studies of mixed polymer monolayers spread at the air/water surface (Gaines 1966, Kwaguchi, 1990, Nagata, 1990, Runge, 1993, Kawaguchi 1997). In particular, (Gabrielli 1971, 1973, 1974, 1980, 1982) have made a significant contribution to the investigation of various mixed polymer films in obtaining information regarding the aspect of their miscibility in the two-dimensional state. One of their vital conclusions is that the miscibility of mixed polymers spread at the air/water interface strongly depends on the interfacial orientation of the polymer chains, such as a predominantly horizontal orientation, with the hydrophobic chains parallel to the interface, and a predominantly vertical orientation, with the hydrophobic chains perpendicular to the interface. The components that show miscibility have the same interfacial orientation, and the immiscible ones have a different orientation.

In general, the miscibility of the mixed polymer monolayers is determined from the plot of the mean areas at a constant surface pressure as a function of composition of one component in the binary mixture. If the plot obeys a linear relationship, i.e. the surface areas are additive, the mixed films can be regarded as an ideal mixture or as a completely immiscible mixture. The deviation from the linear relation stems from the contribution of intermolecular interaction between two components. A negative deviation means that the mixtures are considered to be stable and miscible, whereas a positive deviation indicates that the mixtures are less stable than components alone at the interface.

On the other hand, determining the miscibility of two polymers in the bulk state (polymer blends) is one of the central problems in polymer science and engineering. Few pairs of polymers were found to be miscible (Paul 2000). Not all polymers form stable films at the air/water interface, therefore it is not easy to determine good pairs to compare the miscibility in the bulk state with that in a film spread at the air/water interface. Kawaguchi and coworkers (Kawaguchi 1997) have performed surface measurements on binary mixtures of poly(methacrylate) (PMA) and poly(vinyl acetate) (PVAc) at the air/water interface. Since PVAc/PMA mixtures were immiscible, PMA components were squeezed out and their AFM images strongly depended on

the mixed ratio of PVAc/PMA. Monroy et al.(Monroy 1998) reported a study of monolayers of hydrogen-bonded polymer blends at the air/water interface: poly(vinyl acetate)/poly(4-hydroxystyrene)(P4HS). While PVAc forms extended monolayers, and the free surface of water is found to be a good solvent for it, P4HS forms compressed monolayers, and the surface is a near θ -type solvent for it. PVAc and P4HS form miscible non-ideal monolayers until near the collapse pressure through the whole composition range. Their results correlate well with the miscibility of the corresponding mixtures in the bulk state.

In a previous study(Hsu 2004), the miscibility of stereoregular PMMA with PVAc in the bulk state was investigated in this laboratory. Based upon the results of the prepared blends, casting solvent and tacticity of PMMA have little effect on the miscibility of PMMA with PVAc. PMMA was found to be almost completely immiscible with PVAc. Through the calculation of phase compositions of two immiscible phases, the blends prepared from THF show a little more partial miscibility than the ones cast from chloroform. Among the three tactic PMMAs, isotactic PMMA was found to show the highest mutual solubility with PVAc when the blends were cast from THF.

The aim of this paper is to compare the miscibility of stereoregular PMMA with PVAc in two-dimensional state with that of polymers in the bulk state. We measured the surface pressures of the binary films of stereoregular PMMA/PVAc (the same polymers used previously). On the basis of the results of surface pressure-area per molecule (π -A) isotherms, miscibility between stereoregular PMMA and PVAc was investigated in this article. The effect of tacticity and composition of PMMA on its miscibility with PVAc was expounded and reported in detail in this article. To the best of our knowledge, there is no systematic and detailed report on the miscibility of mixed stereoregular PMMA/PVAc monolayers at the air/water interface.

2. EXPERIMENTAL

2.1 Materials

Isotactic, atactic and syndiotactic PMMAs (designated as i, a and

s-PMMA in this study) were purchased from Polysciences, Inc, Warrington, PA. According to the supplier information, the molecular weights (M_w) of iPMMA, aPMMA and sPMMA are the same about 100,000 g/mol. The molecular weight (M_w) of PVAc is also about 100,000 g/mol. PVAc was mixed with each tactic PMMA individually to form mixtures in the weight ratios of 1/3, 1/1 and 3/1.

The polydispersities (M_w/M_n) of the three PMMAs were not measured therefore not reported here. However, the molecular weight distribution effect is believed to be minimal in the current study when compared with the effect of tacticity. We did not characterize the tacticity of PMMA by NMR. Therefore a simple estimation of the fractions of meso (m) and racemic (r) diads was resorted. The meso diad fractions of PMMA were computed previously(Hsu 1999). The m and r fractions of iPMMA, aPMMA and sPMMA are 68.7% and 31.3%, 33.8% and 66.2%, 9.3% and 90.7%, respectively. The error of estimation is 5-8%. The glass transition temperatures (T_g s) of bulk iPMMA, aPMMA , sPMMA and PVAc were determined to be 75°C, 103°C,122°C and 44°C, respectively, with a DuPont 2000 thermal analyzer at a heating rate of 20 °C/min. The inflection point of the specific heat jump of the second thermal scan was taken as T_g .

2-butanone purchased from Kanto Chemical Co. Inc. was used as the spreading solvent for the polymer films. The solvent was chosen for the continuation of a previous study(Lee 2006). Previously, 2-butanone was used to prepare mixed stereoregular PMMA/P4HS monolayers. Only highly pure water, which was purified by means of a Milli-Q plus water purification system, with a resistivity of 18.2 M Ω -cm was used in all experiments.

2.2 Surface Pressure Measurements

A model minitrough was purchased from KSV Instruments Ltd., Finland. The Teflon trough was 320 mm long and 75 mm wide. Regulation of the trough temperature was controlled by circulating constant temperature water from an external circulator through the tubes attached to the aluminum-based plate of the trough. The trough was placed on an isolated vibration-free table and was enclosed in a glass chamber to avoid contaminants from the air. A

computer with an interface unit obtained from KSV instruments Ltd. was used to control the Teflon barriers. One of the important characteristics of the trough system is that two barriers confining a monolayer at the interface are driven symmetrically during the compression of the monolayer. The surface pressure was measured by the Wilhelmy plate method. The resolution for surface measurement is 0.004 mN/m, and the inaccuracy of surface area regulation is less than 1%, according to the specifications of the instruments. A surface pressure-area per molecule (π -A) isotherm was obtained by a continuous compression of a monolayer at the interface by two barriers. Before each isotherm measurement, the trough and barriers were cleaned with an ethanol solution and then rinsed by purified water. The sand blasted platinum plate used for surface pressure measurements was also rinsed with purified water and then flamed before use. In addition, all glassware was cleaned prior to use in the same manner as the trough and barrier.

For starting the experiment, the freshly cleaned trough was placed into position in the apparatus first, then it was filled with purified water as the subphase with temperatures controlled at $10\pm 0.5^\circ\text{C}$, $25\pm 0.5^\circ\text{C}$ and $40\pm 0.5^\circ\text{C}$. The clean platinum plate was hanged in the appropriate position for surface pressure measurements. The surface pressure fluctuation was estimated to be less than 0.2 mN/m during the compression of the entire trough surface area range. Then, the two barriers were moved back to their initial positions. The sample concentration of solution of polymer and solvent was set at 0.5 mg/mL. A 25 μL sample containing monolayer-forming polymeric materials was spread on the subphase by using a Hamilton microsyringe to make the deposition of polymer molecules at almost the same condition. At least 30-45 min was allowed for evaporation of the spreading solvent. After the solvent was evaporated, the monolayer was compressed continuously at a rate of 3.5 mm/min to obtain a single π -A isotherm. The π -A isotherms of our studied polymers are dependent on the compression rate therefore the results were performed at the same compression speed.

3. RESULTS AND DISCUSSION

3.1 Single Polymer Film

The π -A isotherms of monolayers for the three PMMA stereoisomers and PVAc are shown in Figures 1-3 at 10°C, 25°C and 40 °C, respectively. The discussion for the three stereoisomers at three temperatures was reported previously (Lee 2008) and therefore omitted here. The results are consistent with those reported by (Beredjick 1960).

The π -A isotherms of PVAc (shown in Figures 1-3) at three temperatures were in agreement with literature (Runge 1993, Lee 2002, Kawaguchi 1991). The isotherm of PVAc belongs to the expanded film type. At 10°C, the collapse pressure of PVAc is detectable. However, at 25°C and 40 °C the collapse pressure of PVAc can not be detected likely due to more flexible chain motion at higher temperatures.

3.2 PMMA/PVAc Mixture

Figure 1 presents the π -A isotherms of mixed monolayers for (a) iPMMA/PVAc, (b) sPMMA/PVAc and (c) aPMMA/PVAc at 10°C. Figures 2 and 3 show the π -A isotherms of the same polymers at 25°C and 40 °C, respectively.

For Figure 1(a)-1(c), the π -A isotherms of mixed monolayers at 10°C are located mostly in the middle of corresponding homopolymer isotherms. However, for iPMMA/PVAc(25/75) and aPMMA/PVAc(25/75) their isotherms are shifted even to the left of PVAc isotherm. Therefore negative deviations were obviously observed in these mixed monolayers. The π -A isotherms of mixed monolayers at 25°C shown in Figure 2(a)-2(c) are in the majority located in between corresponding homopolymer isotherms. The only exception is aPMMA/PVAc(25/75) mixed monolayer. Its isotherm is outside of PVAc and aPMMA isotherms and demonstrates smaller surface area than PVAc at the same surface pressure. For Figure 3(a)-3(c), the π -A isotherms of mixed monolayers at 40°C demonstrate quite different behavior from those at 10°C and 25°C. Most isotherms are located either to the left or to the right of homopolymer isotherms. However, the aPMMA/PVAc(25/75) π -A

isotherm is located in the middle of aPMMA and PVAc isotherms.

3.3 The Excess Area

To proceed with a quantitative analysis of the mixed monolayer behavior at the air/liquid surface, the excess area (A_{ex}) should be calculated. At a given surface pressure, the excess area is defined as the difference between the average area per molecule of a mixed monolayer consisting of components 1 and 2 and that of an ideal mixed monolayer (Gaines 1966).

$$A_{ex} = A_{12} - A_{id} = A_{12} - (X_1 A_1 + X_2 A_2) \quad (1)$$

where A_{12} and A_{id} are the mean and ideal areas per molecule of the mixed monolayer at a given surface pressure, respectively, X_1 and X_2 imply the mole fractions of components 1 and 2, respectively, and A_1 and A_2 are the areas per molecule of each pure monolayer at the same surface pressure. Based on eq.(1), the A_{ex} values of mixed PMMA/PVAc monolayers can be estimated from the data shown in Figures 1(a)-1(c), 2(a)-2(c) and 3(a)-3(c), individually.

In Figures 4(a)-4(c), 5(a)-5(c) and 6(a)-6(c) the normalized quantities, A_{ex}/A_{id} are shown as a function of PVAc mole fraction and surface pressure at 10°C, 25°C and 40 °C, respectively. Since the repeat unit of PVAc is smaller than PMMA, the mole fraction is slightly larger than the original weight fraction of 0.25, 0.50 and 0.75. For Figure 4(a)-4(c) the A_{ex}/A_{id} values are all negative at high PVAc mole fractions regardless of stereoregularity. Negative area deviation shows a sign of favorable interaction between PMMA and PVAc. PVAc and PMMA are miscible at 77% PVAc mole composition. For the other two PVAc mole fractions, the A_{ex}/A_{id} values are mostly positive indicating that PVAc and PMMA are less stable than component polymers. For low PVAc mole fraction and at surface pressure of 20 mN/m, aPMMA is miscible with PVAc because of negative excess area.

The A_{ex}/A_{id} values shown in Figure 5(a)-5(c) are in the majority positive indicating PMMA and PVAc are less stable at 25°C than at 10°C. However, aPMMA is miscible with PVAc at high PVAc mole fractions because of the observation of negative A_{ex}/A_{id} values shown in Figure 5(c). For iPMMMA/PVAc and aPMMA/PVAc mixed monolayers, the increase of surface

pressure is beneficial to the decrease of the A_{ex}/A_{id} values.

At 40°C the A_{ex}/A_{id} values of iPMMMA, sPMMA and aPMMA with PVAc are expounded as below. For Figure 6(a), iPMMMA and PVAc are miscible at high PVAc mole fractions because of negative A_{ex}/A_{id} values. For low or mid PVAc compositions in Figure 6(a), the A_{ex}/A_{id} values are mostly positive. For sPMMA and PVAc isotherms shown in Figure 6(b), the A_{ex}/A_{id} values are often positive. The only exception is sPMMA/PVAc monolayers with high PVAc mole fractions and at high surface pressures. The negative A_{ex}/A_{id} values were observed indicating miscibility between sPMMA and PVAc. A quite unusual behavior was observed in aPMMA/PVAc isotherms at 40°C shown in Figure 6(c). At low or high PVAc compositions, the A_{ex}/A_{id} values are negative indicating miscibility between aPMMA and PVAc. However, positive A_{ex}/A_{id} values were observed at mid PVAc compositions. The PVAc/aPMMA monolayers are less stable at mid PVAc compositions. Since around 20mN/m and 40°C PVAc, sPMMA and some mixed monolayers exhibit a plateau, the estimated excess area may have some uncertainty. However, the general trends are similar.

The excess area in this study is likely a function of several variables including stereoregularity of PMMA, temperature, surface pressure, PVAc composition, hydrophobic orientation and interaction, C=O(PMMA) and C=O(PVAc) interaction, hydrophilic interaction in water and others. According to (Gabrielli 1982), PMMA and PVAc have a predominantly horizontal orientation, with hydrophobic chains parallel to the interface. Although PMMA and PVAc have a similar horizontal orientation, they are often immiscible regardless of stereoregularity of PMMA because of unfavorable interaction between PVAc and PMMA. The temperature effect on the excess area does not show any definite trend. The higher the surface pressure like most studies, the excess area becomes more negative. The increasing PVAc composition in the mixed PMMA/PVAc monolayers often causes the excess area to be more negative. The effect of C=O(PMMA) and C=O(PVAc) interaction and hydrophilic interaction in water on the excess area is not understood according to the best of our knowledge.

CONCLUSIONS

Miscibility deduced from the π -A isotherms of mixed stereoregular PMMA/PVAc monolayer correlates approximately with that for the corresponding polymer blends in the bulk state. The DSC study in the bulk state shows that PMMA and PVAc are almost completely immiscible regardless of stereoregularity of PMMA. The mutual solubility between PMMA and PVAc is often close to zero. The results deduced from the π -A isotherms of mixed PMMA/PVAc monolayers show mostly the positive A_{ex}/A_{id} values in agreement with immiscibility between PMMA and PVAc in the bulk state. However, a minor difference was detected on the basis of π -A isotherms. Interestingly, the A_{ex}/A_{id} values were found to be often negative at a high PVAc mole fraction. The miscibility between PVAc and PMMA is therefore proven possible at this composition in the two-dimensional state.

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10°C i-PMMA v.s PVAc

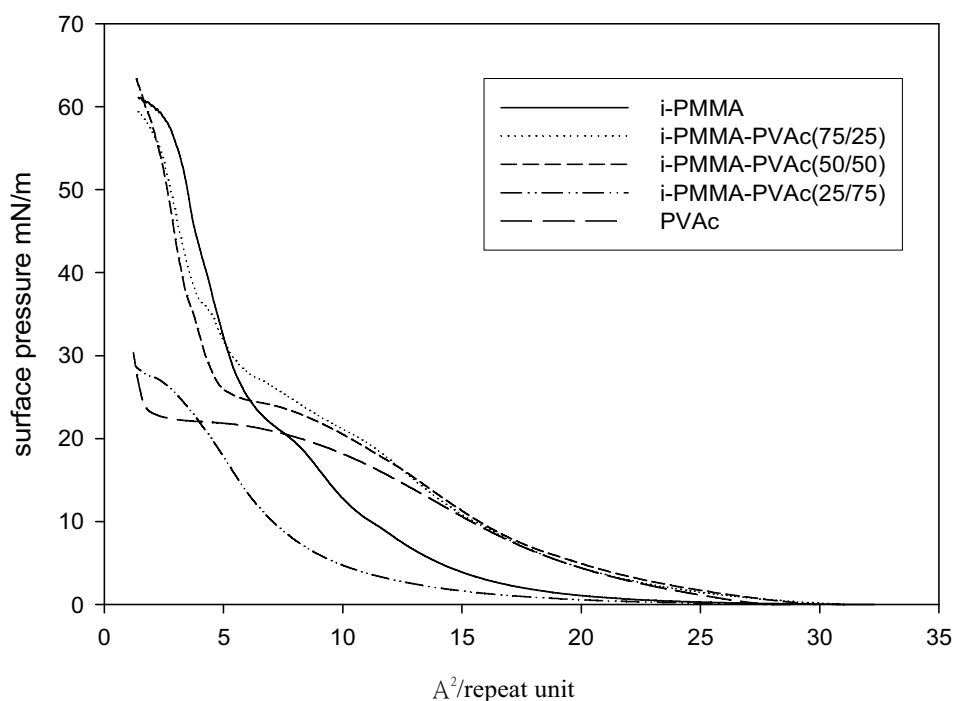


Fig. 1a. Surface pressure-area per molecule isotherms for mixed monolayers of iPMMA/PVAc at 10°C

10°C s-PMMA v.s PVAc

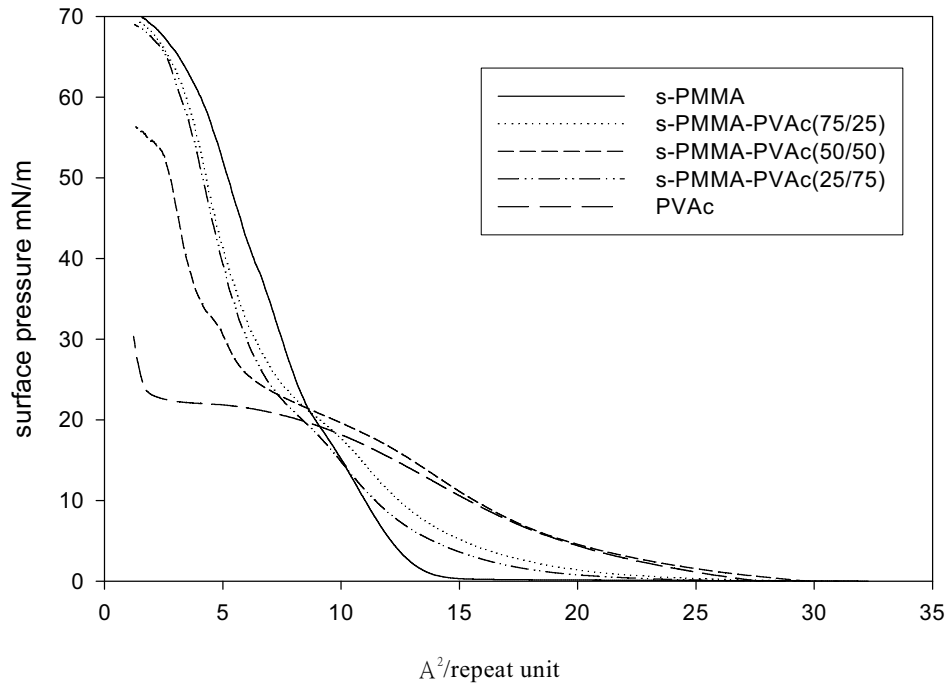


Fig. 1b. Surface pressure-area per molecule isotherms for mixed monolayers of sPMMA/PVAc at 10°C

10°C a-PMMA v.s PVAc

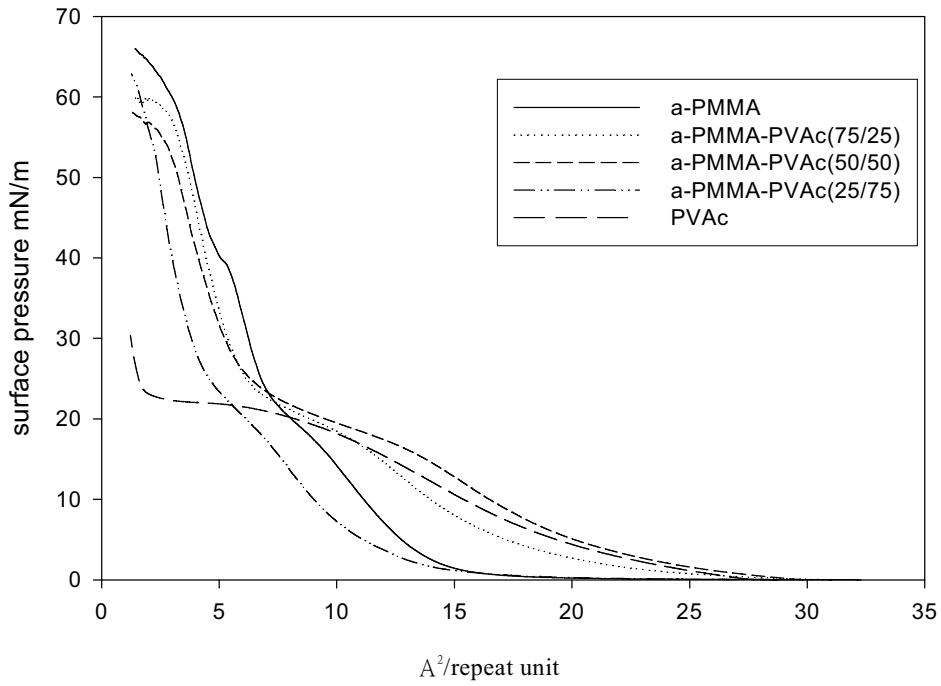


Fig. 1c. Surface pressure-area per molecule isotherms for mixed monolayers of aPMMA/PVAc at 10°C

25°C i-PMMA v.s PVAc

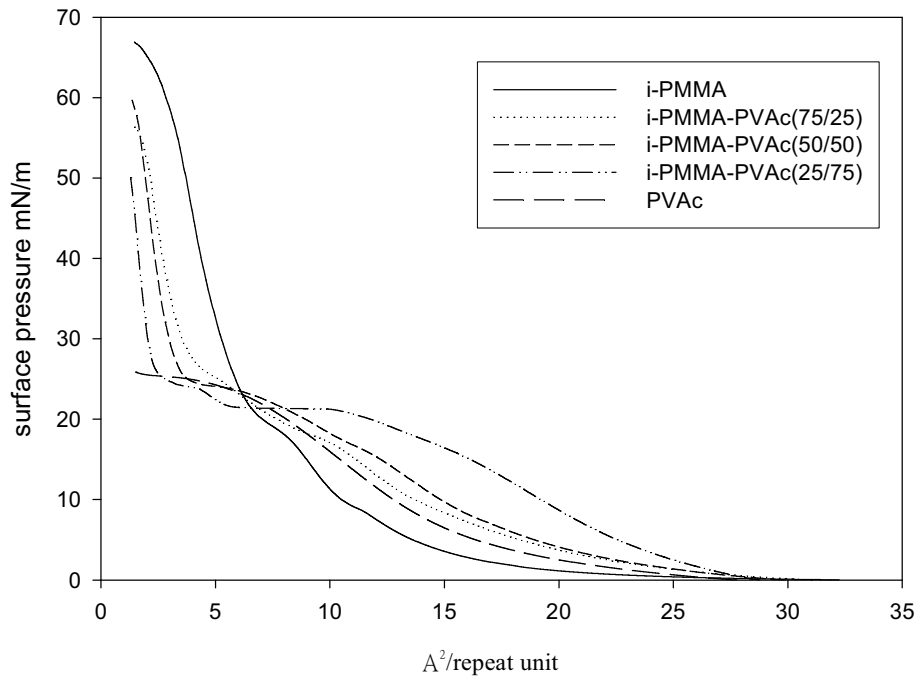


Fig. 2a. Surface pressure-area per molecule isotherms for mixed monolayers of iPMMA/PVAc at 25°C

25°C s-PMMA v.s PVAc

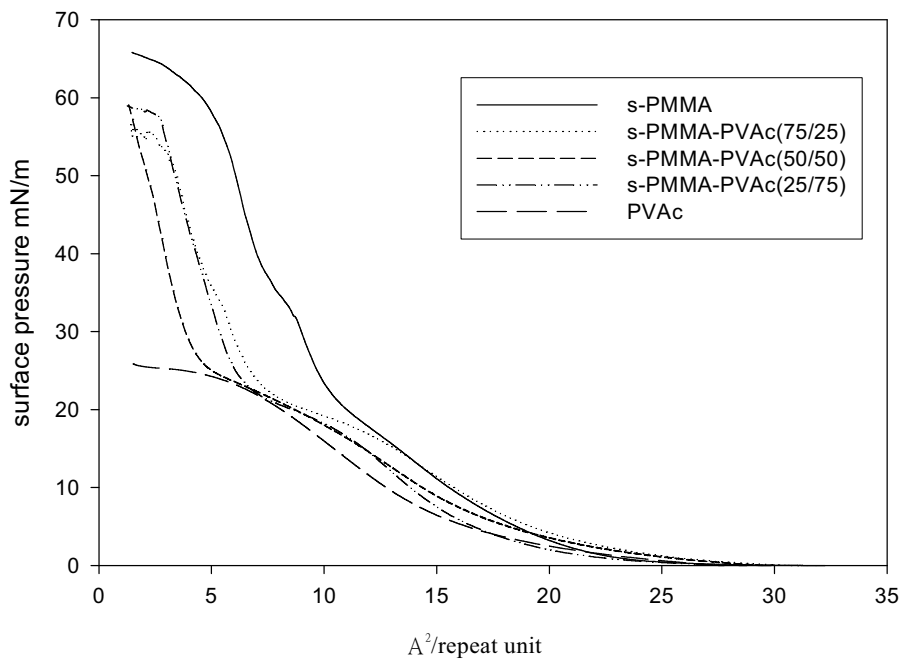


Fig. 2b. Surface pressure-area per molecule isotherms for mixed monolayers of sPMMA/PVAc at 25°C

25°C a-PMMA v.s PVAc

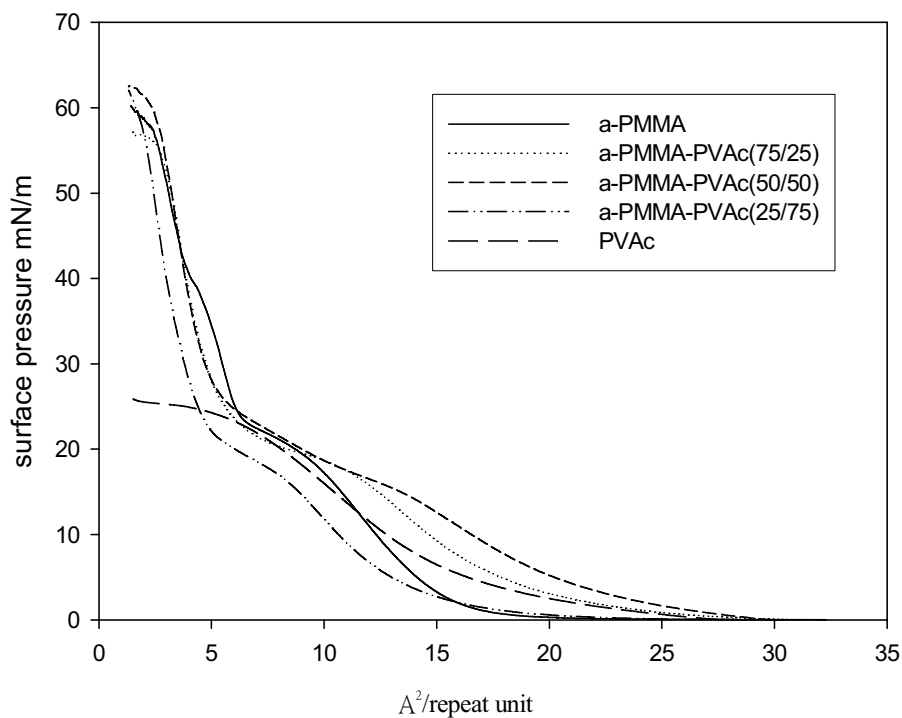


Fig. 2c. Surface pressure-area per molecule isotherms for mixed monolayers of aPMMA/PVAc at 25°C

40°C i-PMMA v.s PVAc

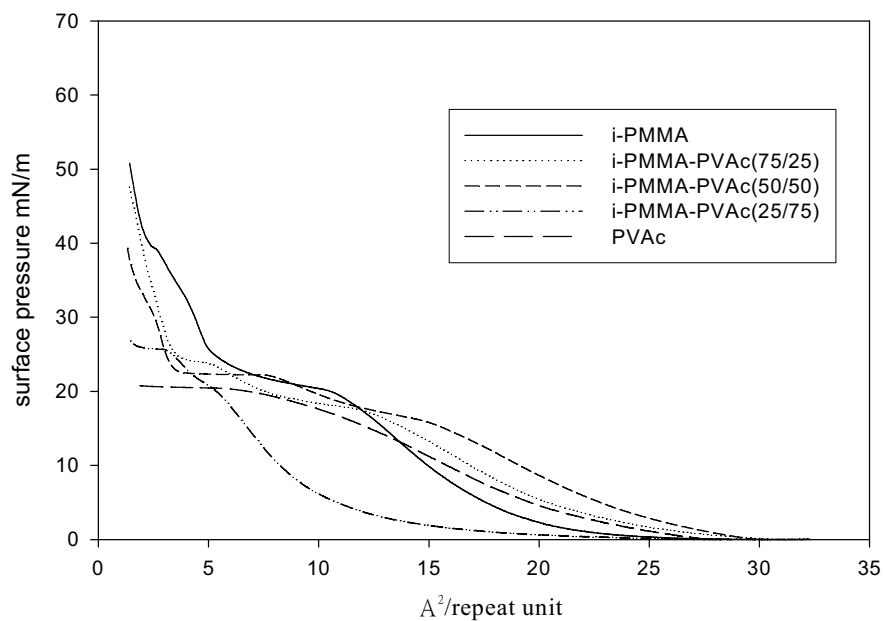


Fig. 3a. Surface pressure-area per molecule isotherms for mixed monolayers of iPMMA/PVAc at 40°C

40°C s-PMMA v.s PVAc

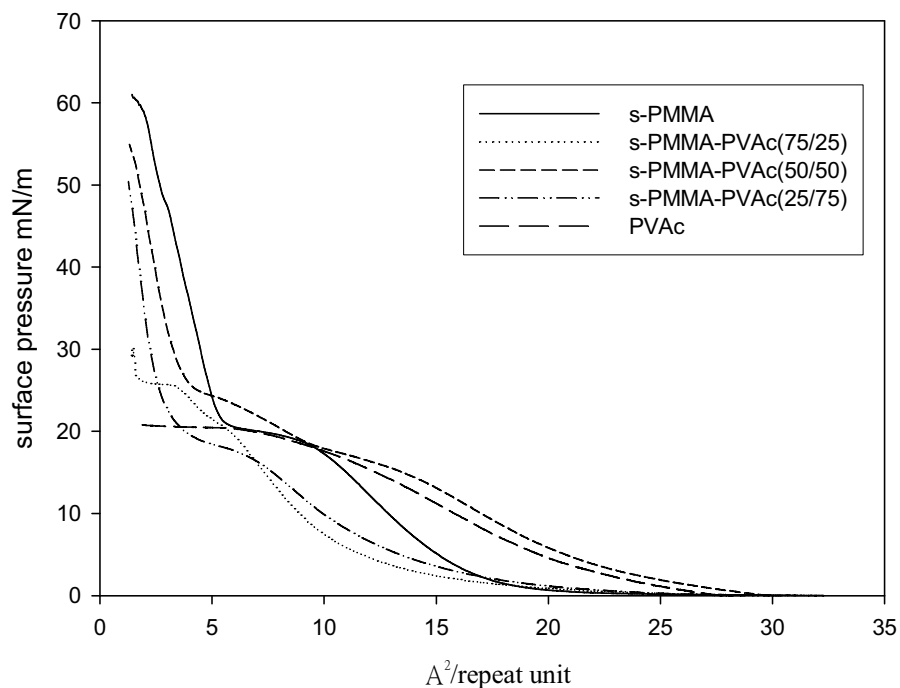


Fig. 3b. Surface pressure-area per molecule isotherms for mixed monolayers of) sPMMA/PVAc at 40°C

40°C a-PMMA v.s PVAc

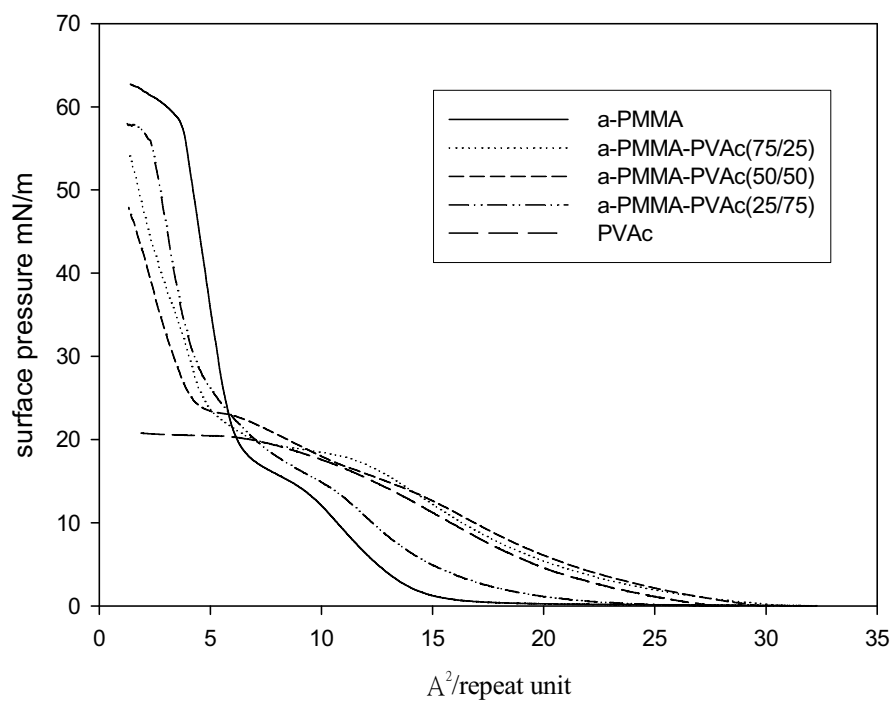


Fig. 3c. Surface pressure-area per molecule isotherms for mixed monolayers of aPMMA/PVAc at 40°C

10°C , $\pi = 5, 10, 20$ iPMMA-PVAc

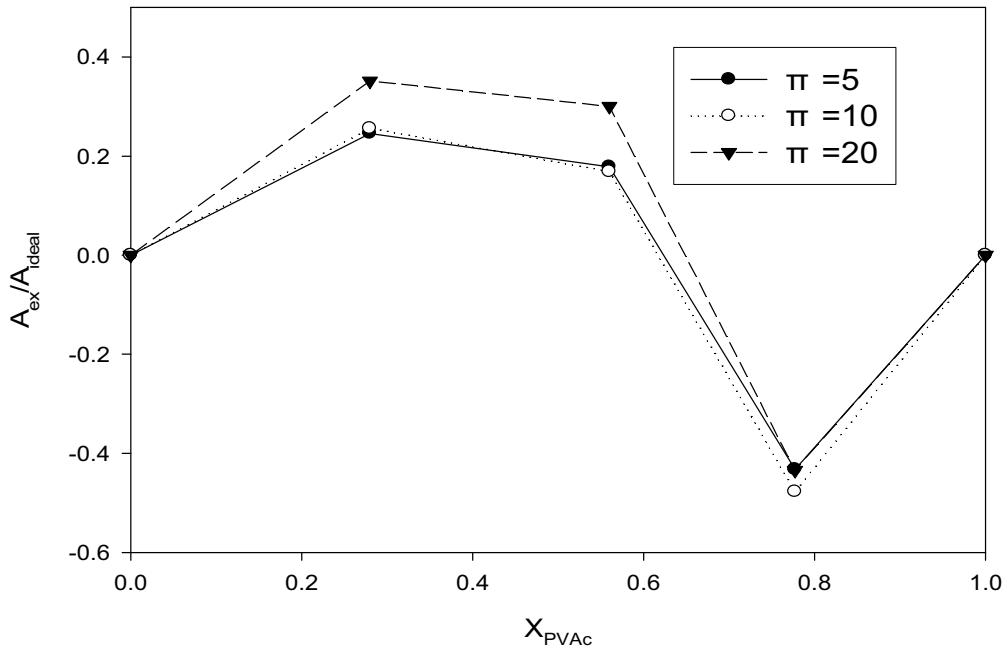


Fig. 4a. A_{ex}/A_{id} as a function of composition for mixed monolayers of iPMMA/PVAc at various surface pressures and 10°C.

10°C , $\pi = 5, 10, 20$ sPMMA-PVAc

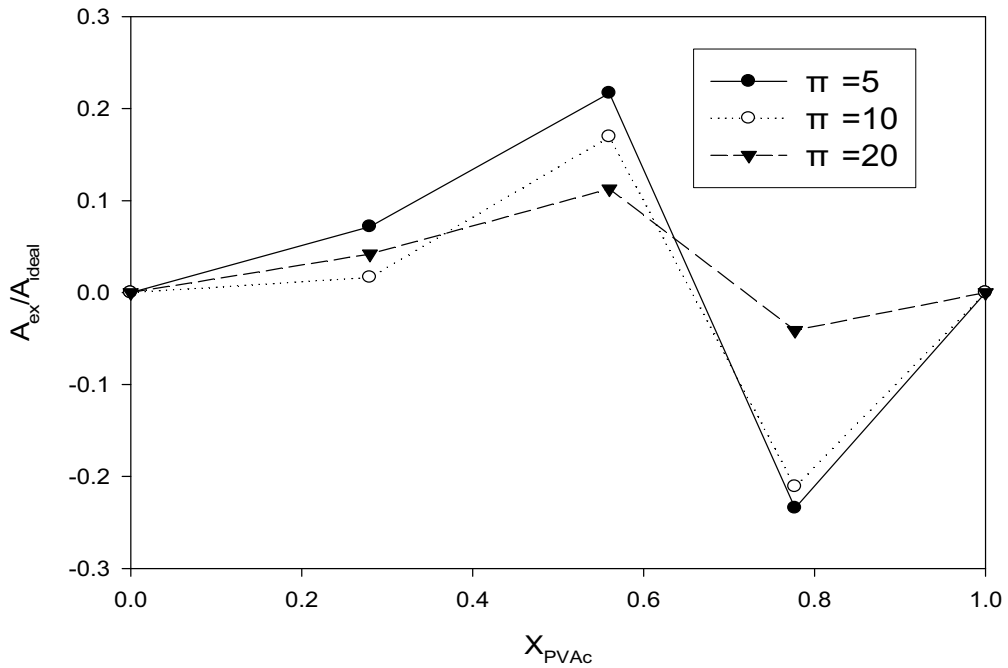


Fig. 4b. A_{ex}/A_{id} as a function of composition for mixed monolayers of sPMMA/PVAc at various surface pressures and 10°C.

10°C , $\pi = 5, 10, 20$ aPMMA-PVAc

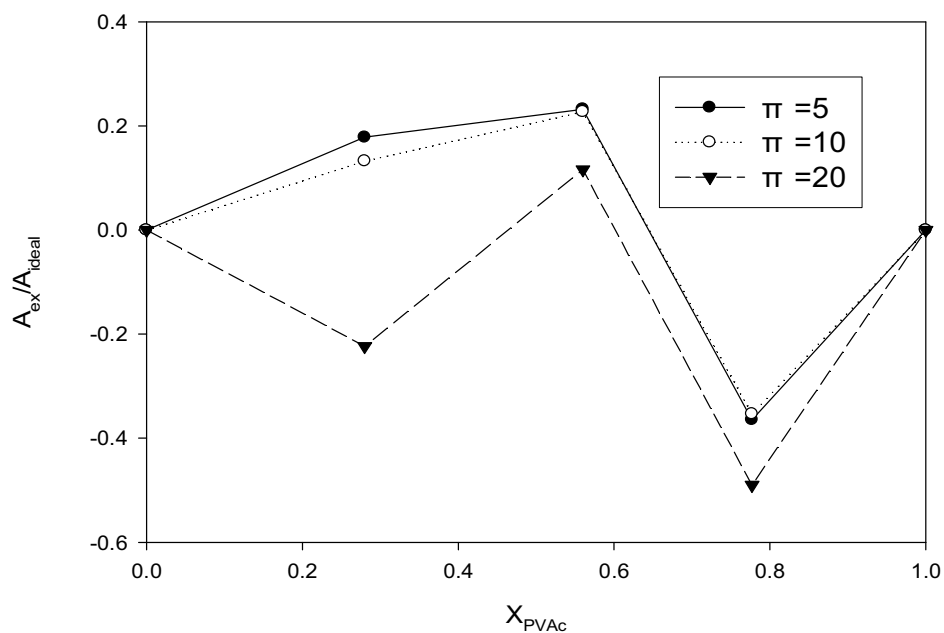


Fig. 4c. A_{ex}/A_{id} as a function of composition for mixed monolayers of aPMMA/PVAc at various surface pressures and 10°C.

25°C , $\pi = 5, 10, 20$ iPMMA-PVAc

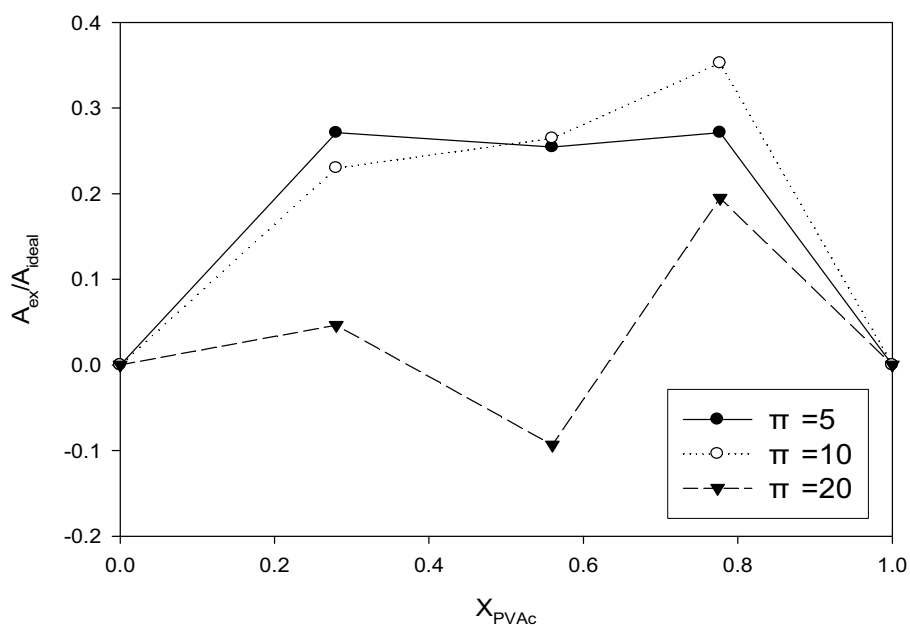


Fig. 5a. A_{ex}/A_{id} for mixed monolayers of iPMMA/PVAc at 25°C.

25°C , $\pi = 5$ 、 10 、 20 sPMMA-PVAc

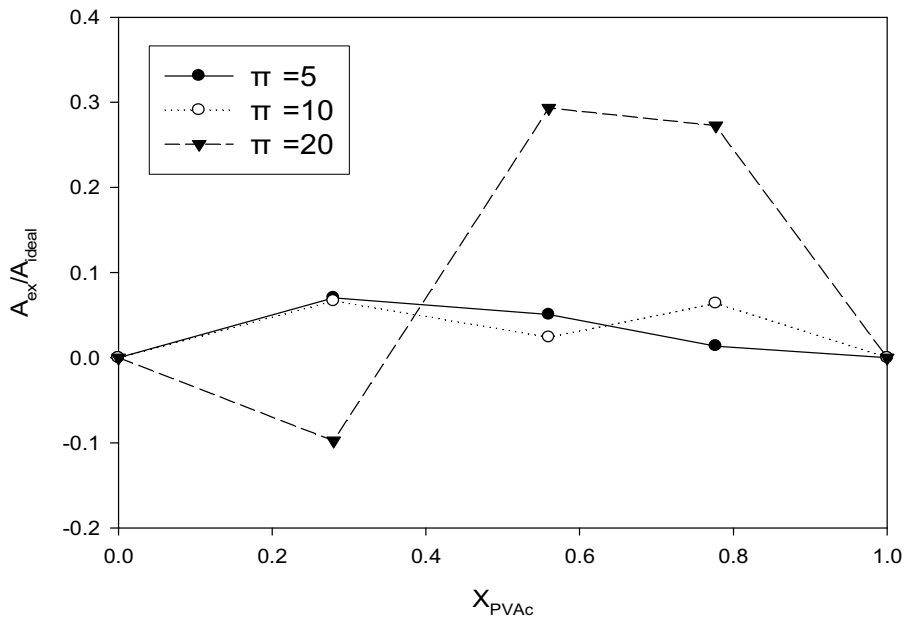


Fig. 5b. A_{ex}/A_{id} for mixed monolayers of sPMMA/PVAc at 25°C .

25°C , $\pi = 5$ 、 10 、 20 aPMMA-PVAc

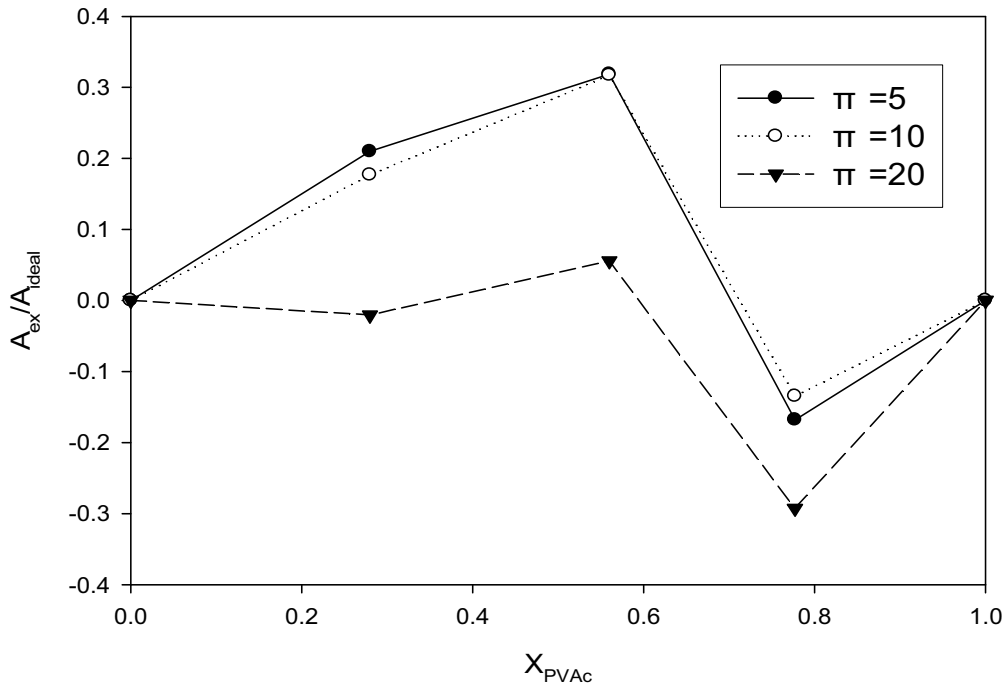


Fig. 5c. A_{ex}/A_{id} for mixed monolayers of aPMMA/PVAc at 25°C .

40°C , $\pi = 5, 10, 20$ iPMMA-PVAc

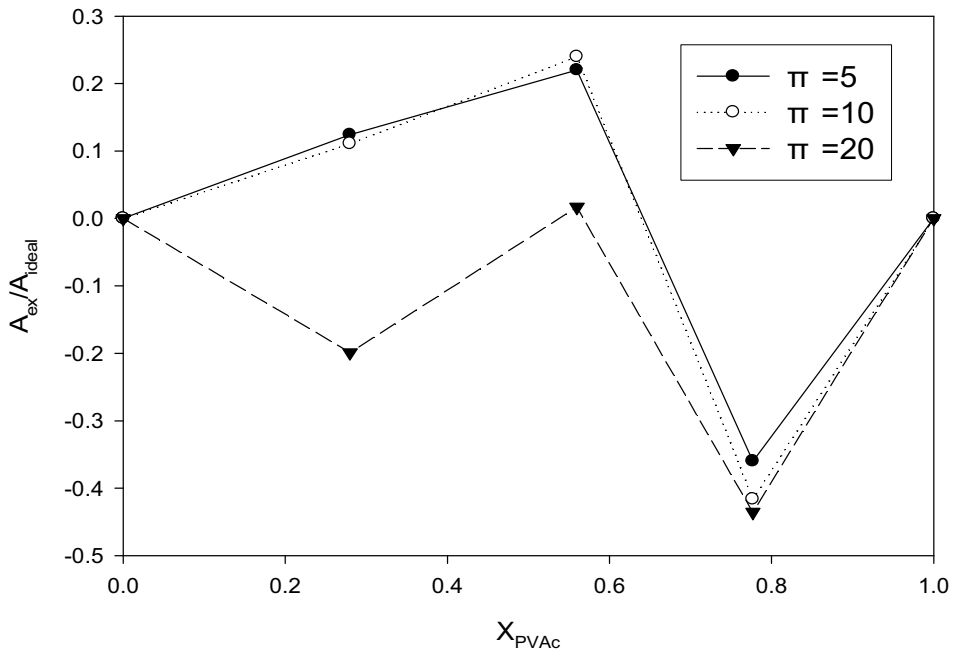


Fig. 6a A_{ex}/A_{id} for mixed monolayers of iPMMA/PVAc at 40°C.

40°C , $\pi = 5, 10, 20$ sPMMA-PVAc

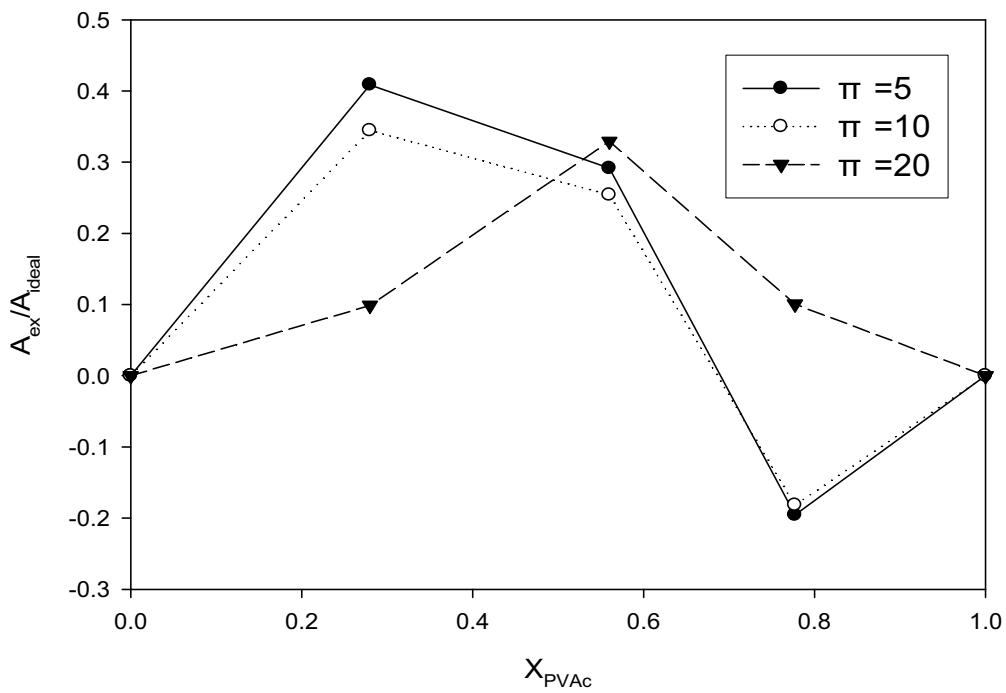


Fig. 6b A_{ex}/A_{id} for mixed monolayers of sPMMA/PVAc at 40°C.

40°C , $\pi = 5$ 、 10 、 20 aPMMA-PVAc

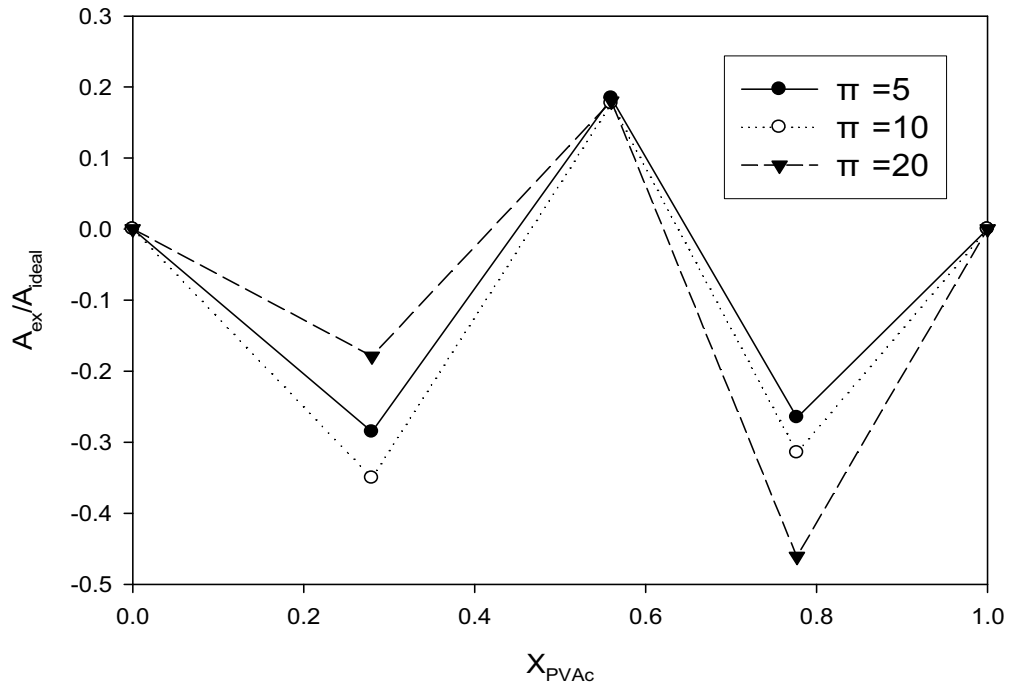


Fig. 6c. A_{ex}/A_{id} for mixed monolayers of aPMMA/